Atomistic Scale Simulation Studies of Ceramic Fuel Forms: FY02

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Summary

Computer modeling has been used to successfully predict the behavior of a range of mononotride materials that are being considered as potential ceramic fuel forms.

Computer modeling using established energy minimization and quantum mechanical techniques were used to study proposed fuel forms and diluents. Several models were created and verified against available experimental lattice data. The models were then used to provide physical properties difficult to obtain experimentally.

The modeling suggests that all these materials are dominated by the Schottky disorder mechanism whereby anion and cation vacancies exist in equilibrium. However, the concentrations of these defects are expected to be very small. Complex defect clusters will also play an important role as will anion deficient nonstoichiometry.

Studies of the incorporation of xenon in several materials suggest that ZrN and TiN will permit smaller concentrations in their lattices than CmN. Thus, values determined from experiments on ZrN and TiN may be used to provide a clear lower bound to the extent of solution in actinides.

Introduction

The focus area for this project is atomic scale computer simulation studies of ceramic fuel forms. The account of work reported here concerns exclusively nitrides, specifically the mononitrides AN. In this context A will be an actinide cation, Cm, Am, Np or Pu: alternatively it can be a cation such as Ti or Zr both of which are being considered as diluents.

This group has extensive past experience in modeling fission product accommodation and transport in uranium oxides fuels. We have modeled the solution and migration of anion species such as iodine and cation species such cesium over the whole range of $UO_{2\pm x}$ stoichiometry [1], described the significance of the redox buffer molybdenum [2] and predicted the energies associated with release of fission gas such as xenon [3]. The experience gained from these previous projects has provided us with an exceptional advantage and perspective when approaching the equivalent problem in nitride fuel forms.

The work described here was started in the middle of FY02 and as such the report details only 6 months activity. Regardless significant progress has been made. As we shall

report, not only have useful models been formulated but also applied to predict, for example, the energies and structures associated with xenon accommodation within the nitride lattices CmN, ZrN and TiN. Particular note should also be given to the reported energies and structures associated with disorder and nonstoichiometry in the diluent TiN, which is also being considered experimentally as a surrogate system.

Methodology

This project calls for the investigation of the properties of actinide nitrides and a number of associated diluent nitride materials. As such we have endeavored to model a wide range of nitride compounds including actinide, lanthanide and transition metal compounds. These materials all form the rocksalt structure (space group Fm3m) thus our aim is to develop and verify our models against available experimental data. We can then use the predictive power of the modeling technique to provide physical properties difficult to access via experimentation. Due to the inherent approximations inevitable in all computer modeling techniques we are primarily concerned with predicting trends. One such trend can be seen in Figure 1, which shows a plot of the experimental lattice parameter of various rocksalt structure nitrides vs. ionic radii [4].
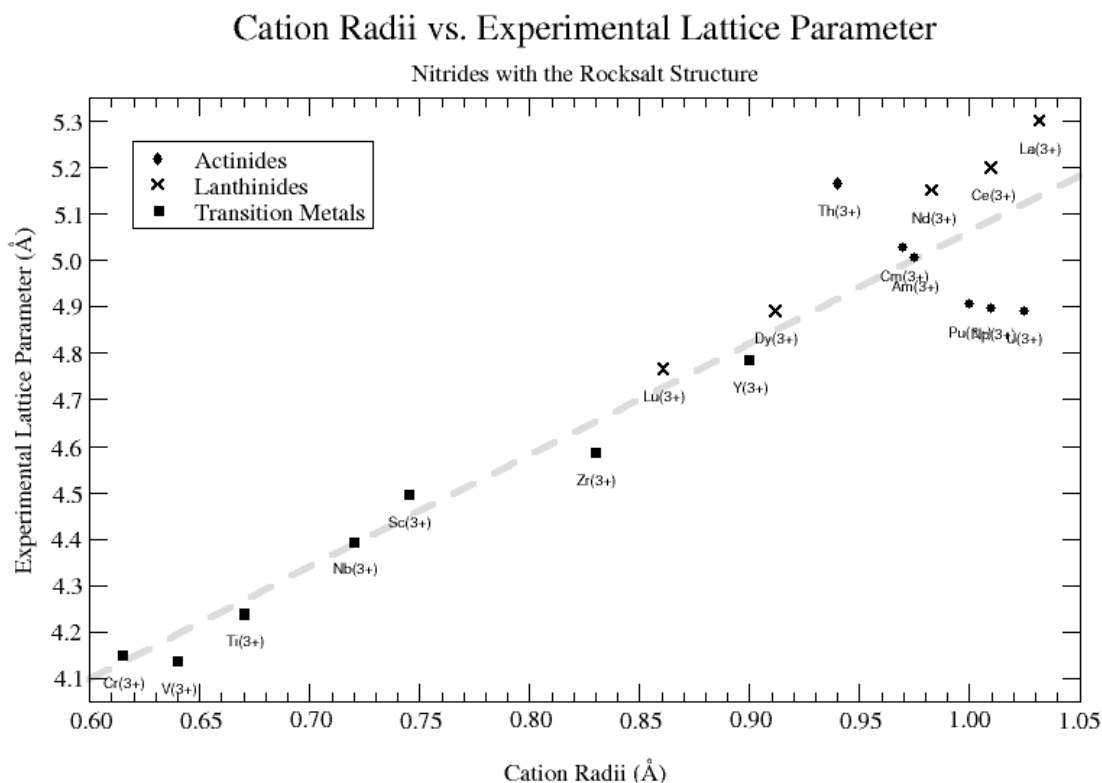

Figure 1: Relationship between cation radii and experimental lattice parameter.

From this we can see that while lanthanide and transition metal lattice parameters scale with ionic radii, actinide nitride lattice parameters do not. This is one trend that we must reproduce.

The primary technique used has been energy minimization, which is based on the Born model of ionic solids [5]. In this model long-range columbic and short-range atomic interactions are included and the energy, E_{ij}, for the interaction between two ions, i and j, takes the form,

$$E_{ij} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + E_{sr}$$

where q is the charge on the ion, r_{ij} is the ion separation and E_{sr} is the short range contribution to the energy. These interactions are summed for a whole lattice to give the lattice energy. A minimization procedure is used to ensure that the simulated lattice is in its lowest energy configuration.

In this study we are interested in the lattice response to defects. This is facilitated by the Mott-Littleton methodology [6], which will be used to calculate point defect energies. Further details can be found in reference [7]. This methodology is implemented in the GULP simulation code [8], which has been used throughout.

The short-range contribution, E_{sr}, is the main variable in the model and great care is taken in its derivation. There are several alternative functional forms for E_{sr}, we have chosen to begin by using the Buckingham potential, which has the form,

$$E_{sr} = A_{ij} \exp\left(\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

where A_{ij}, ρ_{ij} and C_{ij} are variable parameters. We require a set of parameters that allows the simulation of a range of different materials such that reliable comparison can be made between materials. Thus, the parameters must be derived in a self consistent manner. These potential sets can either be derived empirically, by fitting to observable data, or non-empirically, by fitting the potentials to calculated electron density overlap between pairs of ions, or via combination of both to give a semi-empirical potential set.

Non-empirical potentials, derived from calculated electron density overlap, are key to this study since there are only a few pre-existing potentials for nitride materials. Additionally, for simulation of Xe incorporation, a xenon-nitrogen potential would be impossible to derive empirically since no XeN compound is known. We have employed the suite of electron gas codes by Harding and Harker [9] to calculate and fit potentials. Pair potentials can also be derived from the results of more rigorous Quantum Mechanical (QM) simulations.

We have also used a more computationally demanding QM code CASTEP on a limited basis on a borrowed resource. By solving for the wave function of a particular lattice in a specified geometry the total energy and other properties can be derived. We are procuring our own QM resource specifically for this project.

Progress to Date

The Parameterized Lattice Model

Our first task was to establish potential sets that reproduce the experimental lattice parameters. We have developed and verified two such potential sets. One non-empirical set based on electron gas theory and the other, semi-empirical, based on the previous, but fitted to the experimental data and including a shell model for polarisability.

The semi-empirical model is more successful in reproducing experimentally available lattice parameters partly facilitated through the derivation of a shell model to simulate ionic polarisability, thus allowing prediction of dielectric properties. This model consists of a massless shell of charge Y (electronic charges) connected to a core of charge X though an isotropic harmonic spring of force constant k. Thus the charge of an ion is (Y+X). As an isolated ion, the polarizability is given by: Y^2/k. Within the lattice the polarizabilty of an ion is modified through the short range parameterized forces that act between the ion s shell and other surrounding ions. As such, the shell model develops a many body component to the overall lattice model. Here the shell model is specific to the semi-empirical potential set.

When considering incorporation of Xe we can currently only have a non-empirical potential. As such, we report only the non-empirical data, in order to ensure that all our data is self-consistent. Eventually we hope to derive a xenon-nitrogen potential, which is consistent with the semi-empirical potential set.

Predicted Properties and Intrinsic Defect Energies
The reliability of our potential parameters can be assessed by how closely the simulation reproduces the lattice parameter (see Table 1). The bulk elastic tensor has been predicted and is given in Table 2 with predicted bulk modulus. Intrinsic defect energies are important to any atomic process and calculated intrinsic defect energies, and associated disorder reaction energies, per defect, are given in Table 3.

	expt.( )	calc. ( )
CmN	5.027	5.00
DyN	4.890	4.84
ZrN	4.585	4.62
TiN	4.238	4.39

***Table 1: Experimental[10-13] and calculated lattice
parameter for several nitride compounds.***

	C_{11}(GPa)	C_{12}(GPa)	C_{44}(GPa)	Bulk Modulus (GPa)
CmN	430	207	207	281
DyN	495	243	243	327
ZrN	474	308	308	363
TiN	561	388	388	446

Table 2: Calculated elastic tensor and bulk modulus for several nitride compounds.

	Schottky	Anion Frenkel	Cation Frenkel
CmN	8.81	14.14	12.60
DyN	9.19	15.85	12.99
ZrN	7.64	na	10.77
TiN	7.80	16.91	10.88

Table 3: Intrinsic defect and disorder reaction
energies (eV) for several nitride compounds.

Defect energies show that all of these materials are Schottky dominated, however, the formation energies are high, indicating that at the stochiometric composition very few intrinsic defects will exist at equilibrium. Previous work [14] indicated that materials with high intrinsic defect energies are more likely to undergo amorphization under irradiation. As such, these simple nitride materials should not respond well under irradiation. However, all the results presented so far have been for stochiometric materials. TiN, for example, is reported to exhibit significant nitrogen deficient non-stochiometry[15]. Non-stochiometry may well provide sufficient mechanisms for the accommodation and subsequent annealing of irradiation damage.

Fission product solution processes
If we assume that the Xe atoms occupy pre-existing cation vacancy sites the solution (or incorporation [16]) then we predict the energies presented in Table 4.

	Lattice parameter ( )	Solution energy eV	
		Pre-existing site	In equilibrium
CmN	5.027	2.35	11.17
ZrN	4.585	4.00	12.56
TiN	4.238	5.49	13.29

Table 4: Solution energies for Xe in mononitride materials.

As one would expect, in the larger CmN actinide lattice the solution energy is less than in the smaller titanate lattice. Nevertheless, the inert gas atom is large, even in comparison

to Cm, and so the solution energies are high in all three materials. As such, there is a strong thermodynamic driving force for removal of Xe from these materials.

However, this does not necessarily mean that the Xe gas atoms will all be expelled from the lattice. The activation energy for Xe migration through the rock salt lattice is likely to be high and as such Xe could become trapped due to the kinetic or transport barrier. On the other hand, irradiation effects may overcome kinetic barriers and drive the system to thermodynamic equilibrium. Radiation induced resolution of fission products have long been debated in UO_2 fuels [17].

As the amount of Xe builds-up in the system as a whole, the concentration will become such that the equilibrium between the Xe in the trap sites is important. That is, for the Xe atoms to be accommodated in the lattice, cation vacancy sites must be formed. The equilibrium formation energy of a cation vacancy can be derived from;

$$Cm_{cm}^x + N_N^x \rightarrow V_{Cm}^{///} + V_N^{\bullet\bullet\bullet} + CmN \quad \Rightarrow \quad \left\lfloor V_{Cm}^{///} \right\rfloor \left\lfloor V_N^{\bullet\bullet\bullet} \right\rfloor = \exp(E/kT)$$

Since we have previously shown that Schottky disorder is dominant, the concentration of cation vacancies will be approximately the same as the concentration of anion vacancies. Thus,

$$\left\lfloor V_{Cm}^{///} \right\rfloor = \exp(E/2kT)$$

At stoichiometry, the cation vacancy formation energy is therefore half the Schottky energy. The solution energies are thus increased and the equilibrium values are reported in the fourth column of Table 4 above.

Again it is clear that the actinide lattice exhibits a significantly smaller equilibrium solution energy than ZrN or TiN — albeit a large absolute solution energy. Of course, we expect the energies to be overestimates (given the full charge model), but certainly correct relative to each other. We have also assumed that Xe is accommodated at a cation site (by analogy to the situation in UO_2). Nevertheless, the implication is that the equilibrium solution of Xe in the surrogate materials ZrN and TiN will be lower than that exhibited in the actinide lattice. <u>Consequently we predict that the value determined from experiments on surrogate materials will provide a clear lower bound to the extent of solution in actinides.</u> That is, the actinide lattice will be able to accommodate more Xe that the surrogates. Unfortunately it seems that the concentration of Xe, as isolated atomic species, is small. Clearly we should consider the accommodation of Xe at other lattice defects such as nitrogen vacancies and larger defect clusters.

Antisite defect energies
Anti-site defect energies have been calculated initially in TiN. Although this study will be extended to other nitrides, it is anticipated that similar conclusions with be forthcoming. At this point results show that the total formation of single anti-site pairs is a very high energy process: 72.36eV per isolated pair. Despite this, there is a significant

reduction in energy for an associated anti-site pair compared to an isolated anti-site pair: 23.83eV per clustered pair i.e. a binding energy that is 67% of the formation energy.

This may have significant implications for recrystallisation after radiation damage in that it alerts us to the possibility of shear plane or other planar defect formation. Clearly it is necessary to check the energies of such processes by considering larger anti-site cluster formation and possibly planar defect energies. The interface between such larger scale defects and the remaining lattice would provide sites for the accommodation of fission products. It is certainly possible that they would be favorable compared to the high energy isolated defects modeled above.

Improvements to the parameterised lattice model
Despite this improvement, re-evaluation of the electron gas calculation for the common nitrogen-nitrogen potential suggests that the use of a different mathematical form for the interaction potential may be required. Part of the motivation for this stems from the present quantum mechanical calculations on TiN and previous calculations on AlN [18], which are both consistent with an overall 1- charge state for nitrogen. As such, electron gas calculations will be re-run assuming a 1- charge state. This will produce another pair potential set, which will be used alongside the existing pair potential sets for comparison. As is always the case with models based on interatomic potentials we are concerned that overall conclusions do not alter greatly between the models.

Once the quantum mechanical code is working on our local system it will also be a matter of priority to derive a nitrogen-nitrogen pair potential consistently from QM simulations of a nitride lattice. The process used will be equivalent to that described in reference 19.

Nonstoichiometry of TiN

Quantum Mechanical (QM) calculations have been used to predict the variation in lattice parameter with TiN_{1-x} nonstochiometry. The agreement with experimental data is excellent (see Figure 2) and as such we believe that this approach will yield useful results for this project.
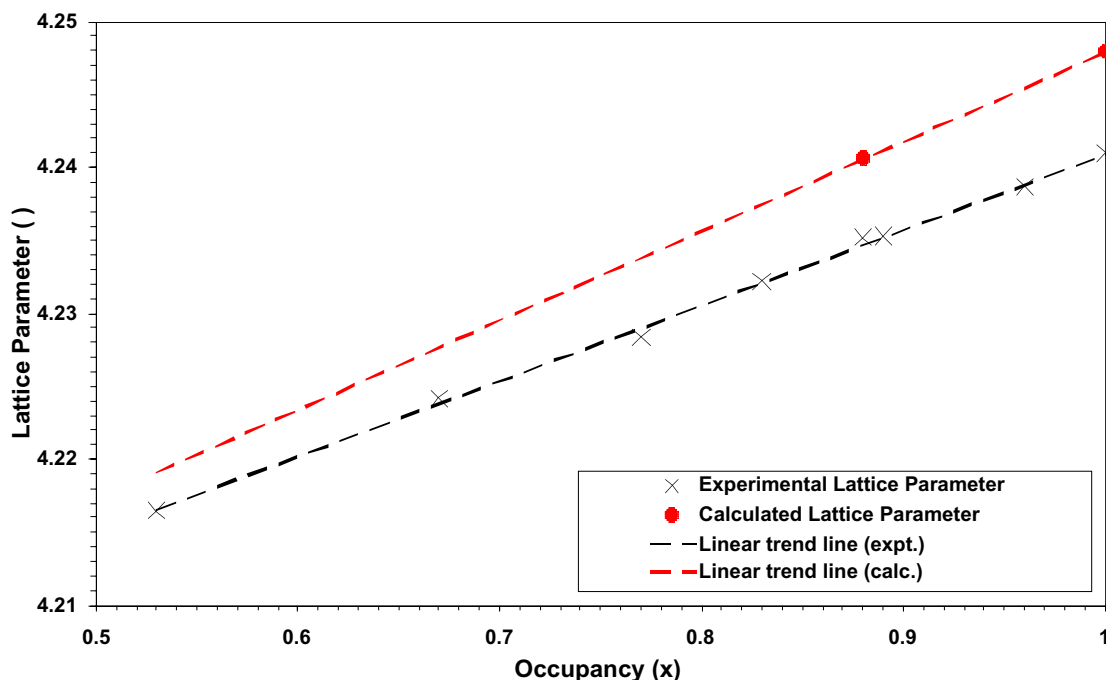
Figure 2: Predicted and experimental lattice parameters in TiN$_{1-x}$.

From this initial study it is clear that TiN exhibits a remarkably broad range of nonstoichiometry. This has implications for the solution of Xe since a nonstoichiometric material will provide alternative solution sites.

Procurement of quantum mechanical code

We have ordered a three-year license for the quantum mechanical code CASTEP from Accelrys with associated visualize and interface modules. This is the same code that we were able to use on a limited basis to model nonstoichiometry in TiN. We are also in the process of procuring additional computing resource to run the CASTEP code on a dedicated parallel cluster.

Conclusions

Parameterized energy minimization and quantum mechanical modeling techniques have been used to successfully simulate the lattice behavior of a range of mononitride materials being considered as potential ceramic fuel forms.

Some physical properties have been predicted and simulations suggest the dominant intrinsic defect mechanism is Schottky disorder. Other more complex defect mechanisms have also been investigated.

Antisite defects have been shown to form strong associates, which may be significant in recrystalisation mechanisms and the propensity for planar defect formation. Large-scale

planar defects may well provide low energy sites for accommodation of fission products and this should be investigated.

TiN is known to have a large anion deficient nonstochiometry range. A methodology has been established which accurately predicts the lattice parameter variation with nonstichiometry.

The incorporation of xenon into CmN, ZrN and TiN has been studied. Results suggest that ZrN and TiN will tolerate smaller concentrations of xenon than CmN. Thus, values determined from experiments on ZrN and TiN may be used to provide a clear lower bound to the extent of solution in actinides.

Several areas remain where further work is necessary. There is still scope to refine the parameters of the energy minimization model. This should lead to more accurate predictions. The acquisition of our own quantum mechanical resource is imminent and will permit further nonstochiometry predictions.

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